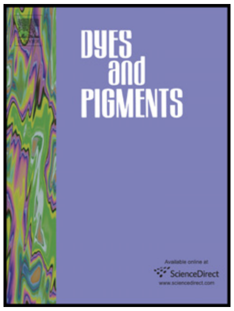

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Synthesis of phenyltetraene chromophores-based hybrid materials for large nonlinear optical activity

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Abstract: Two new chromophores, **CLDS1** and **CLDS2**, based on a similar D-π-A structure as the phenyltetraene chromophore **CLD**, but with an alkylthio group perpendicular to the direction of the long molecular axis as isolation spacer were synthesized. Through a urethane forming reaction between 3-isocyanatopropyltriethoxysilane (ICTES) and chromophores, the alkoxysilane dyes were synthesized. Subsequently, a series of transparent and homogeneous inorganic-organic hybrid films were prepared via a sol-gel process of the alkoxysilane dye with triethoxyvinylsilane. The molecular structures of the resultants were confirmed by ^{1}H NMR, FTIR and UV-visible spectra. After electric poling, the nonlinear optical coefficients (d_{33}) of the hybrid films **F-CLDS1** and **F-CLDS2** were determined to be 104.54 and 98.17 pm V^{-1}, respectively, which are almost 3 times the d_{33} value of hybrid film containing **CLD** (37.78 pm V^{-1}), indicating that the incorporation of alkylthio group can efficiently improve the macroscopic optical nonlinearities of hybrid materials.

Keywords: nonlinear optics; phenyltetraene chromophore; isolation group; inorganic-organic hybrid; thin films; sol-gel

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1. Introduction

Second-order nonlinear optical (NLO) materials have received considerable attention due to their wide applications in all-optical switching, fast optical communications, and electro-optic modulation [1-2]. Compared with NLO inorganic crystals, organic NLO polymers display many advantages including large nonlinear optical coefficients, low dielectric constants, fast response time and excellent processing [1-9]. However, the thermal instability of poling-induced chromophore dipole alignment of the poled polymers limits their practical applications in EO devices. Linking the chromophores via covalent bonds onto a highly rigid matrices or cross-linkable polymers can effectively stabilize the dipole orientation. Recently, inorganic-organic hybrid NLO materials through sol-gel process have been considered to be one of the most potential matrix candidates for stabilizing poled dipole orientation [10-19]. By incorporating the NLO active chromophores into the inorganic silica networks, the resulting inorganic-organic materials may display high optical transparency, good thermal stability, and excellent NLO properties. Moreover, the inorganic silica matrix provides an inert environment for organic chromophores and theoretically will prevent damage induced by corona discharge poling and thermal decomposition [20-22].

To achieve large NLO activity, the rational molecular designs of dipole chromophores are crucial and have been demonstrated in a series of conjugated push-pull molecules. Among these molecular systems, the phenyltetraene conjugated bridges attached with terminal strong acceptors, such as **FTC**- and **CLD**-type chromophores, represents one of the most effective chromophores that result in large hyperpolarizability (β) [23-25]. However, the polymers doped with **FTC**- and **CLD**-chromophores tend to lower the NLO response at higher doping content because of the strong dipole–dipole interactions among the chromophore moieties. According to the site-isolation principle, the introduction of some isolation groups to the chromophores is a very promising approach to decrease the dipole-dipole interactions and increase the poling efficiency [26, 27]. Indeed, Dalton and Jen have demonstrated a series of dendritic polymers with **FTC-** and **CLD**-chromophores for significantly enhanced optical nonlinearities [28, 29]. However, there are very few reports concerning the phenyltetraene chromophores linked hybrid materials. In addition, how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of hybrid materials receives little attention.

In this report, we design and synthesize two new chromophores, **CLDS1** and **CLDS2**, based on a similar D-π-A structure as the chromophore **CLD**, but with an alkylthio group perpendicular to the direction of the long molecular axis as isolation spacer (Fig. 1). The chromophore **CLDS1** and **CLDS2** have a comparable β value, but differ in the position of the hydroxyl group, enabling them to be covalently anchored in silica matrix by their donor end or by their isolation spacer. Herein, we report the preparation and structural characterizations of the chromophore-linked hybrid materials, and discuss the influence of isolation group and anchoring position on NLO properties.

2. Experimental Section

2.1 Materials and measurements

All commercially available starting chemicals were purchased and used as received. Tetrahydrofuran (THF) was dried over molecular sieves (3A). Chromophore **CLD** was synthesized as reported [23].

UV-visible absorption spectra were collected with a Hitachi U-4100 spectrometer. Infrared specra were recorded by using a vector 22 Fourier transform infrared spectrometer (Bruker) in KBr disks. ^{1}H NMR spectra of compounds were measured on a Bruker Avance DMX500 spectrometer. Elemental analyses were taken from a Thermo Finnigan Flash EA1112 microelemental analyzer. The thickness of hybrid films was collected via a Tencor alpha-step 200 surface profiler. Thermogravimetric analysis (TGA) was performed with a TA Instruments SDT Q600 at a heating rate of 10 ^{o}C min^{-1} and under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was studied using a Netzsch Instruments 200 F3 with a heating rate of 10 ^{o}C min^{-1} in a nitrogen atmosphere. In situ second harmonic generation (SHG) measurements of the poled films were taken using a Q-switched Nd:YAG laser at 1064 nm and a Y-cut quartz crystal as the Reference.

2.2 Synthesis of chromophore CLDS1 and CLDS2

2-(butylthio)-3-(4-((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethylcyclohex-2-enone (1a). 1a was synthesized according to a literature procedure [30].

3-(4-(diethylamino)styryl)-2-(2-hydroxyethylthio)-5,5-dimethylcyclohex-2-enone (1b). To a sodium ethylate (105 mmol) in ethanol (100 mL) was added mercaptoethanol (7.00 mL, g, 100 mmol), and the solution was stirred for 15 min followed by the addition of isophorone oxide. The solution became dark immediately and was stirred for 30 min to form intermediate 2-((2-hydroxyethyl)thio)-3,5,5-trimethylcyclohex-2-enone, and then 4-(diethylamino)-benzaldehyde (110 mmol) was added and vigorously stirred at 70 ^{o}C for 12 h. The mixture was cooled to room temperature and extracted with dichloromethane, and purified by chromatography using AcOEt/DCM=1/6. ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm): 7.92 (d, J=16.1 Hz, 1H), 7.47 (d, J=8.9 Hz, 2H), 7.08 (d, J=16.1 Hz, 1H), 6.66 (d, J=8.9 Hz, 2H), 3.56 (t, 3H), 3.41 (q, 4H), 2.82 (t, 2H), 2.66 (s, 2H), 2.45 (s, 2H), 1.20 (t, 6H), 1.09 (s, 6H).

3-(4-((2-(tert-butyldimethylsilyloxy)ethyl)(methyl)amino)styryl)-2-(butylthio)-5,5-dimethylcyclohex-2-enone (2a). 1a (7.90 g), imidazole (2.57 g) and *tert*-butylchlorodimethylsilane were mixed in DMF (30 mL), and the solution was stirred for 30 min and poured into saturated NH_4Cl solution. The product was extracted with AcOEt and purified by chromatography (PE/AcOEt=30/1) to yield orange oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.93 (d, J=16.2 Hz, 1H), 7.46 (d, J=8.8 Hz, 2H), 7.00 (d, J=16.2 Hz, 1H), 6.69 (d, J=8.8 Hz, 2H), 3.79 (t, 2H), 3.53 (t, 2H), 3.06 (s, 3H), 2.74 (t, 2H), 2.63 (s, 2H), 2.42 (s, 2H), 1.46 (m, 2H), 1.42 (m, 2H), 1.09 (s, 6H), 0.88 (m, 12H), 0.02 (s, 6H).

2-(2-(tert-butyldimethylsilyloxy)ethylthio)-3-(4-(diethylamino)styryl)-5,5-dimethylcyclohex-2-enone (2b). In a similar manner described above, **2b** was synthesized as a red oil (68%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.90 (d, J=16.2 Hz, 1H), 7.47 (d, J=8.8 Hz, 2H), 7.00 (d, J=16.2 Hz, 1H), 6.65 (d, J=8.8 Hz, 2H), 3.70 (t, J=7.2 Hz, 2H), 3.40 (q, J=7.1 Hz, 4H), 2.87 (t, J=7.2 Hz, 2H), 2.61 (s, 2H), 2.41 (s, 2H), 1.19 (t, J=7.0 Hz, 6H), 1.08 (s, 6H), 0.87 (s, 9H), 0.02 (s, 6H).

2-(3-(4-((2-(tert-butyldimethylsilyloxy)ethyl)(methyl)amino)styryl)-2-(butylthio)-5,5-dimethylcyclohex-2-enylidene)acetonitrile (3a). To a mixture of NaH (4.52 g, 60 wt%, 113 mmol) in THF (100 mL) at 0 ^{o}C was added diethyl cyanomethylphosphonate (17 mL) dropwise by syringe. After the solution clear, **2a** (16.46 g, 32.8 mmol) in THF (30 mL) was added to above solution and the solution was refluxed for 14 h. The product was extracted with AcOEt, evaporated and purified by chromatography (ethyl acetate/petroleum ether=1/30) to yield yellow oil (3.94 g, 23%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.89 (d, J=16.3 Hz, 1H), 7.43 (d, J=8.9 Hz, 2H), 6.86

(d, J=16.2 Hz, 1H), 6.70 (d, J=8.9 Hz, 2H), 6.25 (s, 1H), 3.80 (t, J=6.0 Hz, 2H), 3.53 (t, J=6.1 Hz, 2H), 3.06 (s, 3H), 2.59 (s, 2H), 2.58 (t, J=7.0 Hz, 2H), 2.49 (s, 2H), 1.50 (m, 2H), 1.43 (m, 2H), 1.03 (s, 6H), 0.90 (m, 12H), 0.03 (s, 6H). 48 H (48H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 158.8, 149.9, 149.1, 134.8, 128.9, 126.7, 124.8, 124.4, 119.6, 112.0, 94.6, 60.7, 54.8,43.6, 41.7, 39.4, 35.4, 32.0, 30.4, 28.2, 26.1, 22.1,18.4, 13.9, -5.2.

2-(2-(2-(tert-butyldimethylsilyloxy)ethylthio)-3-(4-(diethylamino)styryl)-5,5-dimethylcyclohex-2-enylidene)acetonitrile (3b). In a similar manner described above, **3b** was synthesized as an orange oil (71%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.85 (d, J=1H), 7.42 (d, 2H), 6.86 (d, 1H), 6.66 (d, 2H), 6.26 (s, 1H), 3.69 (t, 2H), 3.41 (q, 4H), 2.70 (t, 2H), 2.58 (s, 2H), 2.48 (s, 2H), 1.20 (t, 6H), 1.03 (s, 6H), 0.89 (s, 9H), 0.04 (s, 6H).

2-(3-(4-((2-(tert-butyldimethylsilyloxy)ethyl)(methyl)amino)styryl)-2-(butylthio)-5,5-dimethylcyclohex-2-enylidene)acetaldehyde (4a). To a **3a** (3.94 g, 7.5 mmol) in toluene (50 mL) at -78 ^{o}C was added DIBAL-H (20 mL, 1M in hexane, 20 mmol) dropwise. The solution was stirred for 1 h at this temperature, warmed at -40 ^{o}C for 30 min, added with AcOEt (5 mL) and water (20 mL), and vigorously stirred at room temperature for 8h after another AcOEt (50 mL) was added. The alumina gel was filtered off by filtration and the solution was dried over rotary evaporator, and was purified by chromatography (AcOEt/PE=1/25-2/20) to yield red oil (2.51g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 10.16 (d, J=8.1 Hz, 1H), 7.99 (d, J=16.3 Hz, 1H), 7.44 (d, J=8.9 Hz, 2H), 7.03 (d, J=8.0 Hz, 1H), 6.87 (d, J=16.3 Hz, 1H), 6.69 (d, J=8.9 Hz, 2H), 3.80 (t, J=6.0 Hz, 2H), 3.52 (t, J=6.0 Hz, 2H), 3.05 (s, 3H), 2.75 (s, 2H), 2.56 (t, J=7.2 Hz, 2H), 2.52 (s, 2H), 1.49 (m, 2H), 1.40 (m, 2H), 1.05 (s, 6H), 0.88 (m, 12H), 0.03 (s, 6H).

2-(2-(2-(tert-butyldimethylsilyloxy)ethylthio)-3-(4-(diethylamino)styryl)-5,5-dimethylcycloh

ex-2-enylidene)acetaldehyde (4b). In a similar manner described above, **4b** was synthesized as a red oil (54%). ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm): 10.15 (d, J=8.0 Hz, 1H), 7.95 (d, J=16.2 Hz, 1H), 7.43 (d, J=8.8 Hz, 2H), 7.01 (d, J=8.1 Hz, 1H), 6.87 (d, J=16.2 Hz, 1H), 6.66 (d, J=8.8 Hz, 2H), 3.69 (t, J=7.2 Hz, 2H), 3.41 (q, J=7.1 Hz, 4H), 2.75 (s, 2H), 2.71 (t, J=7.2 Hz, 2H), 2.51 (s, 2H), 1.21 (t, J=7.1 Hz, 6H), 1.05 (s, 6H), 0.87 (s, 9H), 0.02 (s, 6H).

2-(4-((1E,3E)-3-(3-(4-((2-(tert-butyldimethylsilyloxy)ethyl)(methyl)amino)styryl)-2-(butylthio)-5,5-dimethylcyclohex-2-enylidene)prop-1-enyl)-3-cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (5a). To a solution of **4a** (2.45 g, 5.57 mmol) and 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (1.33 g, 6.69 mmol) in CH$_2$Cl$_2$ (50 mL) was added AcOH (0.1 mL) and piperidine (0.2 mL) mixture. The solution was stirred at room temperature for 4 h, dried and purified by chromatography (CH$_2$Cl$_2$) to yield dark blue solid (2.30 g, 58%). m.p.: 157 and 206 ^{o}C. T$_d$ (95 wt%): 260 ^{o}C. ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm): 8.11 (t, J=13.5 Hz, 1H), 8.03 (d, J=16.1 Hz, 1H), 7.52 (d, J=12.2 Hz, 1H), 7.45 (d, 8.9 Hz, 2H), 6.95 (d, J=16.1 Hz, 1H), 6.70 (d, J=9.0 Hz, 2H), 6.39 (d, J=14.8 Hz, 1H), 3.80 (t, J=5.9 Hz, 2H), 3.54 (t, J=5.9 Hz, 2H), 3.07 (s, 3H), 2.59 (t, J=7.2 Hz, 2H), 2.55 (s, 2H), 2.50 (s, 2H), 1.70 (s, 6H), 1.53 (m, 2H), 1.43 (m, 2H), 1.03 (s, 6H), 0.88 (m, 12H), 0.02 (s, 6H).

2-(4-((1E,3E)-3-(2-(2-(tert-butyldimethylsilyloxy)ethylthio)-3-(4-(diethylamino)styryl)-5,5-dimethylcyclohex-2-enylidene)prop-1-enyl)-3-cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (5b). In a similar manner described above, **5b** was synthesized as a dark solid (0.55 g, 58%). ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm): 7.15 (t, J=13.5 Hz, 1H), 8.00 (d, J=15.7 Hz, 1H), 7.52 (d, J=12.1 Hz, 1H), 7.45 (d, J=8.1 Hz, 2H), 6.96 (d, J=16.1 Hz, 1H), 6.67 (d, J=7.5 Hz, 2H), 6.37 (d, J=15.0 Hz, 1H), 3.73 (t, J=6.9 Hz, 2H), 3.43 (q, J=6.8 Hz, 4H), 2.74 (t, J=6.9 Hz, 2H), 2.55 (s, 2H), 2.51 (s, 2H), 1.70 (s, 6H), 1.22 (t, J=6.9 Hz, 6H), 1.03 (s, 6H), 0.89 (s, 9H), 0.04 (s, 6H). Anal. Calcd. for $C_{34}H_{38}N_4O_3S$ (582.76): C, 70.07; H, 6.57 ; N, 9.61. Found: C, 69.91; H, 6.61; N, 9.50.

2-(4-((1E,3E)-3-(2-(butylthio)-3-(4-((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethylcyclohex-2-enylidene)prop-1-enyl)-3-cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (CLDS1). To the **5a** (2.05, 2.89 mmol) solution in acetone (50 mL) was added dilute HCl (4.30 mL, 1.2 N, 5.16 mmol). The solution was stirred overnight and diluted with water (100 mL) and neutralized with potassium carbonate, the precipitation was collected as a dark blue powder (1.68 g, 98%). m.p. (with decomposition): 232 ^{o}C. T_d (95 wt%): 254 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.08 (t, J=13.5 Hz, 1H), 8.03 (d, J=16.2 Hz, 1H), 7.50 (d, J=12.3 Hz, 1H), 7.47 (d, J=8.8 Hz, 2H), 6.95 (d, J=16.1 Hz, 1H), 6.78 (d, J=8.9 Hz, 2H), 6.39 (d, J=14.8 Hz, 1H), 3.87 (q, J=5.7 Hz, 2H), 3.58 (t, J=5.6 Hz, 2H), 3.08 (s, 3H), 2.58 (t, J=7.2 Hz, 2H), 2.53 (s, 2H), 2.50 (s, 2H), 1.71 (s, 6H), 1.66 (t, J=5.9 Hz, 1H), 1.52 (m, 2H), 1.43 (m, 2H), 1.04 (s, 6H), 0.88 (t, J=7.3 Hz, 3H).

2-(3-cyano-4-((1E,3E)-3-(3-(4-(diethylamino)styryl)-2-(2-hydroxyethylthio)-5,5-dimethylcyclohex-2-enylidene)prop-1-enyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (CLDS2). In a similar manner described above, chromophore **CLDS2** was synthesized as a green powder (86%). m.p.: 246 ^{o}C. T_d (95 wt%): 252 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.14 (t, J=13.5 Hz, 1H), 8.00 (d, J=15.8 Hz, 1H), 7.51 (d, J=12.1 Hz, 1H), 7.46 (d, J=7.7 Hz, 2H), 6.98 (d, J=16.0 Hz, 1H), 6.67 (d, J=8.2 Hz, 2H), 6.39 (d, J=14.8 Hz, 1H), 3.70 (t, J=6.0 Hz, 2H), 3.42 (q, J=6.8 Hz, 4H), 2.81 (t, J=5.9 Hz, 2H), 2.57 (s, 2H), 2.51 (s, 2H), 1.70 (s, 6H), 1.22 (t, J=7.0 Hz, 6H), 1.04 (s, 6H). Anal. Calcd. for $C_{35}H_{40}N_4O_2S$ (580.78): C, 72.38; H, 6.94; N, 9.65. Found: C, 72.23; H, 6.93; N, 9.60.

2.3 Synthesis of alkoxysilane dye ICTES-CLD, ICTES-CLDS1 and ICTES-CLD2

ICTES-CLD. To the solution of **CLD** (0.40 g, 0.79 mmol) in dry THF (6 mmol) were added Tin (II) 2-ethylhexanoate (3 drops) and 3-isocyanatopropyltriethoxysilane (**ICTES**, 0.45 g, 1.82 mmol). After the mixture was stirred at 65 ^{o}C for 8 h, the solution was cooled to room temperature was added to petroleum ether (150 mL) and a lot of precipitation occurred. The precipitation was collected by filtration and purified by chromatography using AcOEt/petroleum ether=1/1 as eluents to yield 0.24 g of dark blue solid (0.32 mmol, 41%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.01-8.29 (m, 1H), 7.39 (t, 2H), 6.71-6.86 (m, 4H), 6.25-6.38 (m, 3H), 4.92 (s, 1H), 4.23 (t, 2H), 3.82 (q, 6H), 3.63 (t, 2H), 3.18 (q, 2H), 3.05 (s, 3H), 2.42 (t, 4H), 1.69 (d, 6H), 1.26 (m, 9H), 1.05 (d, 6H), 0.62 (t, 2H).

ICTES-CLDS1. In a similar manner described above, **ICTES-CLDS1** was synthesized as a dark blue solid (71%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.06 (m, 2H), 7.51 (d, J=12.2 Hz, 1H), 7.46 (d, J=8.3 Hz, 2H), 6.94 (d, J=16.1 Hz, 1H), 6.74 (d, J=8.0 Hz, 2H), 6.39 (d, J=14.8 Hz, 1H), 4.94 (s, 1H), 4.24 (s, 2H), 3.82 (q, 6H), 3.64 (s, 2H), 3.17 (d, 2H), 3.06 (s, 3H), 2.57 (m, 4H), 2.50 (s, 2H), 1.71 (s, 6H), 1.62 (m, 2H), 1.53 (m, 2H), 1.43 (m, 2H), 1.23 (q, 9H), 1.03 (s, 6H), 0.88 (s, 3H), 0.62 (t, 2H).

ICTES-CLDS2. In a similar manner described above, **ICTES-CLDS2** was synthesized as a blue solid (54%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.11 (d, J=12.3 Hz, 1H), 8.00 (d, J=16.2 Hz, 1H), 7.49 (d, J=12.4 Hz, 1H), 7.46 (d, J=8.6 Hz, 2H), 6.96 (d, J=16.0 Hz, 1H), 6.67 (d, J=8.3 Hz, 2H), 6.40 (d, J=14.8 Hz, 1H), 4.87 (t, J=5.1 Hz, 1H), 4.12 (t, J=6.7 Hz, 2H), 3.81 (q, J=7.0 Hz, 6H), 3.43 (q, J=6.8 Hz, 4H), 3.10 (q, J=6.3 Hz, 2H), 2.82 (t, J=6.6 Hz, 2H), 2.56 (s, 2H), 2.51 (s, 2H), 1.71 (s, 6H), 1.24 (m, 15H), 1.04 (s, 6H), 0.59 (t, J=8.1 Hz, 2H).

2.4 Preparation of Hybrid Films

The alkoxysilane dyes (0.1 mmol) were mixed with triethoxyvinylsilane (VTES, 1.9 mmol) in THF, and then 8 mmol acidic water (pH=1) was added. The solutions were kept stirring for 12 hours and aged for another 4 days. Then the solutions were filtered through 0.22 μm filter and spin-coated on clean indium tin oxide (ITO) glass substrate to afford blue organic-inorganic hybrid films.

3. Results and Discussion

3.1 Synthesis and Characterization

The detailed synthetic procedure of chromophores was presented in Scheme 1. The chromophore **CLDS1** was synthesized start from a nucleophilic substitution of epoxyisophorone with alkanethiol, giving a thiol-substituted isophorone. Horner-Emmons olefination followed by DIBAL-H reduction converted dienone **2a** into aldehyde **4a**. Knoevenagel condensation of the 2-cyanomethylene-3-cyano-4, 5, 5-trimethyl-2, 5-dihydrofuran to aldehyde **4a** was performed to yield **5a**, and then the deprotection procedure of **5a** produced hydroxyl-functionalized chromophore **CLDS1**. In the synthesis of the analogous chromophore **CLDS2**, 2-mercaptoethanol was selected to react with epoxyisophorone to introduce hydroxyl group at the side of chromophore. These chromophores were further reacted with 3-isocyanatopropyltriethoxysilane to give alkoxysilane dyes via a urethane forming reaction [31-33]. Following the hydrolysis and copolymerization process of the alkoxysilane dyes and triethoxyvinylsilane, a series of inorganic-organic hybrid film were prepared.

The structures of chromophores and alkoxysilane dyes were confirmed by ^{1}H NMR and FTIR spectroscopy. All the spectral assignments clearly support the proposed structure. The peaks assigned to vinylic protons of alkoxysilane dye **ICTES-CLD** illustrate the presence of cis- and trans-isomer mixtures of the dye, while for **ICTES-CLDS1** and **ICTES-CLDS2**, protonic peak with a coupling constant 14.8 Hz at 6.38 ppm show the all-trans double-bond configuration of derived tetraene alkoxysilanes which could provide a better conjugation and increase the hyperpolarizability of the dyes significantly.

The IR spectra of chromophore **CLDS1**, alkoxysilane dye **ICTES-CLDS1** and hybrid film **F-CLDS1** are shown in Fig. 2. In terms of chromophore **CLDS1**, the absorption of cyano group in acceptor 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran appears at 2220 cm^{-1}, and the characteristic absorption band at 3430 cm^{-1} is assigned to stretching vibration of the hydroxyl group. Compared with **CLDS1**, the presences of the secondary amino group and carbonyl group indicate that alkoxysilane dye **ICTES-CLDS1** was obtained from the coupling reaction between hydroxyl groups in chromophore and isocyanate group in ICTES. For hybrid film **F-CLDS1**, the significantly increased broad absorption band around 1080 cm^{-1} and decreased ethyl group absorption around 2900 cm^{-1} suggests the formation of Si-O-Si network due to the hydrolysis and condensation of Si-O-R.

UV-vis absorption spectra of chromphores in $CHCl_3$ indicate that chromophore **CLD** has a maximum absorption wavelength (λ_{max}) of 661 nm, and **CLDS1** almost exhibits the same absorption band with a λ_{max} at 662 nm, indicating that the butylthio substituent does not affect the molecular D-π-A structure. Compared with chromophore **CLD** and **CLDS1**, the λ_{max} of chrmophore **CLDS2** shifts bathochromicly to 691 nm, which can be explained by the variation of donor group in **CLDS2**. As shown in Fig. 3, the shapes of absorption bands the hybrid films

F-CLDS1 and **F-CLDS2** are similar but broader to the corresponding chromophores in solution, indicating that the chromophores have been successfully incorporated in the silica networks. The broadening of absorption bands in films can attributed to the fact that chromophores exhibit more vibrational and rotational in the complex environment of silica matrix than in pure solution.

The thermal stability of the chromophores and hybrid materials are measured by thermogravimetric analysis. As shown in Fig. 4, the decomposition temperature (T_d) of chromophores **CLDS1** and **CLDS2** are 254 and 252 ^oC, respectively. The hybrid films **F-CLDS1** and **F-CLDS2** show the decomposition temperatures at 270 and 257 ^oC, respectively. This implies that the inorganic silica backbone can indeed improve the thermal stability of chromophores.

3.2 Nonlinear optical properties

The $\beta_{CT}\mu_g$ values of chromophores were measured by solvatochromic method [15, 31]. As shown in Table 1, the chromophore **CLD** shows a $\beta_{CT}\mu_g$ value of 6967.9×10^{-30} esu·D, while the chromophore **CLDS1** and **CLDS2** exhibit a larger $\beta_{CT}\mu_g$ value of 7207.6 and 7976.8×10^{-30}esu·D, respectively. This indicates that the introduction of alkylthio substituent can enhance the $\beta_{CT}\mu_g$ value because the auxiliary π-accepting alkylthio group can make the chromophores have better conjugation [30]. Except of the enhancement of $\beta_{CT}\mu_g$ value, it is expected that the alkylthio side group will affect the poling efficiency and the macroscopic NLO response of hybrid materials. To investigate the substituent effect on NLO properties of hybrid materials, the films **F-CLD**, **F-CLDS1** and **F-CLDS2** were poled at 5.5 kV dc voltage from 120 to 160 ^oC for half an hour and the second order NLO properties were characterized by in situ SHG measurement. The SHG coefficients (d_{33}) were calculated by equations according to the references [34] and summarized in Table 2. The experimental data were collected at 1064 nm fundamental wavelength, and considering the severe absorption at the doubling frequency 532 nm, absorption correction was applied.

The d_{33} values of hybrid films **F-CLD**, **F-CLDS1** and **F-CLDS2** are 37.78, 104.54 and 98.17 pm V^{-1}, respectively. Compared with the film **F-CLD**, the film **F-CLDS1** shows about 3 times enhancement of d_{33} value. The significantly enhanced macroscopic optical nonlinearities of **F-CLDS1** could be attributed to the fact that by adding an alkylthio group perpendicular to the conjugated backbone at the center of the bridge, not only it can improve the $\beta_{CT}\mu_g$ value, but also serve as an efficient isolation spacer to reduce the interchromophore electrostatic interactions. It needs to be mentioned that the film **F-CLDS2**, in which the chromophore **CLDS2** was covalently linked to silica matrix, also exhibits an excellent NLO property. This clearly shows that the enhancement of NLO response is mainly attributed to the incorporation of alkylthio group as isolation spacer, while scarcely be influenced by anchoring position of chromophore. It may provide an efficient approach to design and synthesize new hybrid materials for large optical nonlinearity.

For the purpose of determining the temperature at which dipolar relaxation of SHG signal is halved, a thermal dynamic induced depoling experiment was performed while the half-decay temperature ($T_{d/2}$) was used as notation (Fig. 5). As shown in Table 1, the hybrid film **F-CLDS2** has a highest half-decay temperature of 127 ^{o}C. This behavior could be rationalized by the more difficult dipole orientation in hybrid film **F-CLDS2**, indicating that the side-on chromophore attachment geometry can enhance the thermal stability of NLO properties in comparison with end attachment model.

4. Conclusion

Two new chromophores, **CLDS1** and **CLDS2**, based on a similar D-π-A structure as the phenyltetraene chromophore **CLD**, but with an alkylthio group perpendicular to the direction of the long molecular axis as isolation spacer were synthesized. By anchoring the chromophores in inorganic silica matrix, a series of hybrid materials were prepared. Due to the incorporation of alkylthio group, the hybrid films **F-CLDS1** and **F-CLDS2** exhibit a significantly enhanced d_{33} value of 104.54 and 98.17 pm V^{-1}, respectively, which are almost 3 times the d_{33} value of hybrid film containing **CLD**. Furthermore, the film **F-CLDS2** shows a quite high thermal stability of optical nonlinearity. This result could provide an efficient approach to design and synthesize new hybrid materials for large optical nonlinearity.

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Table 1 Solvatochromic data and hyperpolarizabilities of the chromophores

Chromophore	$\lambda_{max}{}^{a}$ (nm)	ε (10^4 $mol^{-1}\cdot L\cdot cm^{-1}$)	$\Delta\nu_{1/2}$ (cm^{-1})	$\lambda_{max}{}^{b}$ (nm)	$\Delta\nu$ (cm^{-1})	a nm	$\beta_{CT}\cdot\mu_g$ (10^{-30}esu·D)
CLD	669	3.32	4762	626	1026	1.1	6967.9
CLDS1	667	3.08	5099	622	1085	1.1	7207.6
CLDS2	673	3.41	5617	633	939	1.1	7976.8

[a] measured in DMF [b] measured in 1,4-dioxane

Table 2 Nonlinear optical property of hybrid films.

Hybrid film	λ_{max}(nm)	d_{33}(pm/V)	$T_{d/2}{}^{a}$(^{o}C)
F-CLD	599	37.78	110
F-CLDS1	635	104.54	102
F-CLDS2	666	98.17	112

[a] Half-decay temperature of d_{33} value.

Figure Captions

Scheme 1. Synthetic route of alkoxysilane dyes **ICTES-CLDS1** and **ICTES-CLDS2**

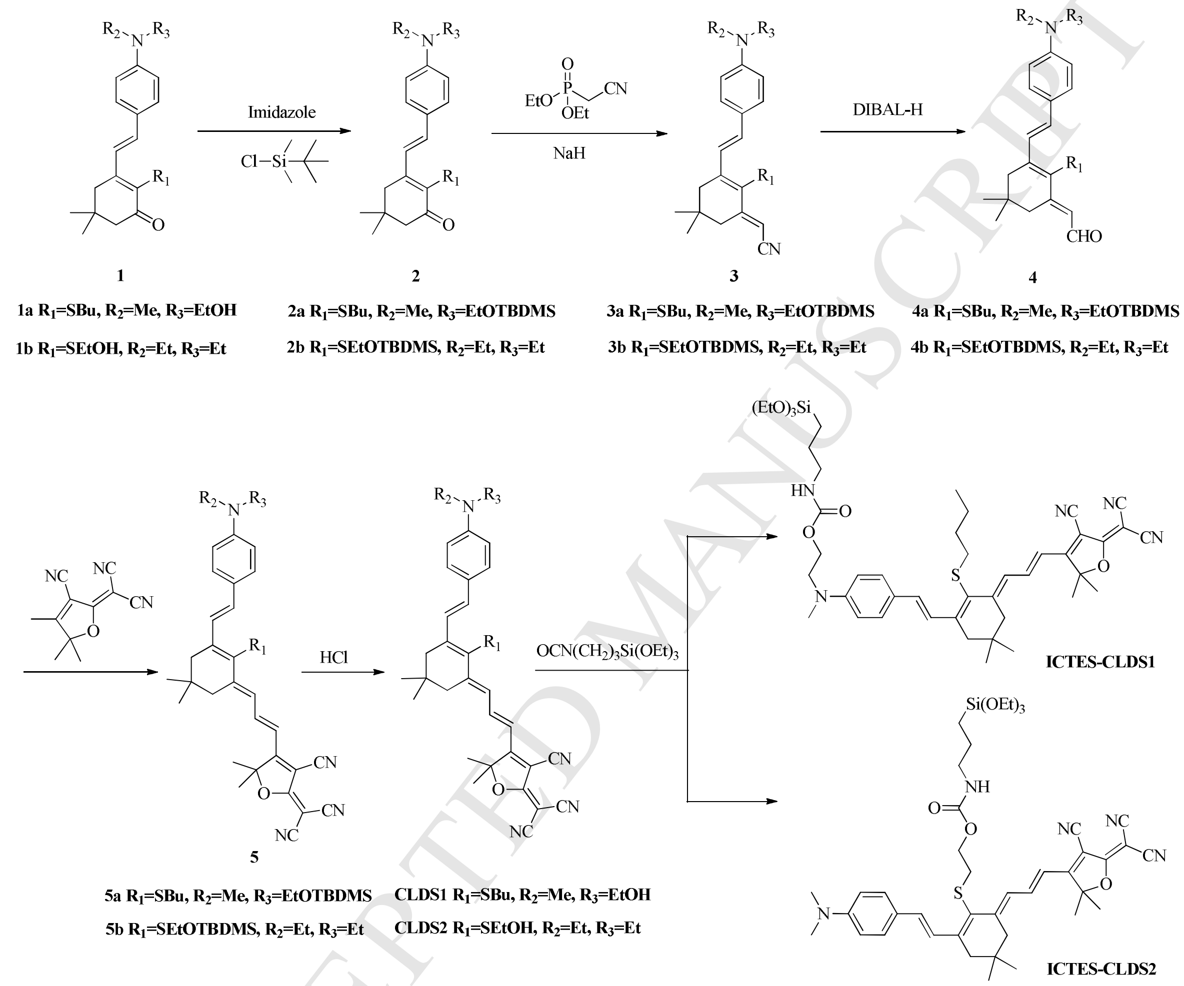
Fig. 1. Structures of the chromophores **CLD**, **CLDS1** and **CLDS2**

Fig. 2. FT-IR spectra of **CLDS1**, **ICTES-CLDS1** and film **F-CLDS1**

Fig. 3. UV-vis spectra of chromophores in $CHCl_3$ and hybrid films

Fig. 4. TGA curves of chromophores and hybrid films

Fig. 5. Decay of the normalized d_{33} values as a function of temperature for film **F-CLDS2**.



1a R$_1$=SBu, R$_2$=Me, R$_3$=EtOH

1b R$_1$=SEtOH, R$_2$=Et, R$_3$=Et

2a R$_1$=SBu, R$_2$=Me, R$_3$=EtOTBDMS

2b R$_1$=SEtOTBDMS, R$_2$=Et, R$_3$=Et

3a R$_1$=SBu, R$_2$=Me, R$_3$=EtOTBDMS

3b R$_1$=SEtOTBDMS, R$_2$=Et, R$_3$=Et

4a R$_1$=SBu, R$_2$=Me, R$_3$=EtOTBDMS

4b R$_1$=SEtOTBDMS, R$_2$=Et, R$_3$=Et

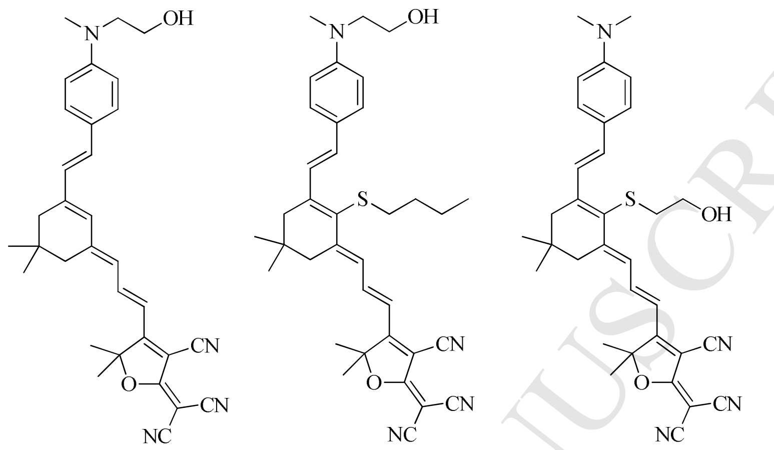
5a R$_1$=SBu, R$_2$=Me, R$_3$=EtOTBDMS

5b R$_1$=SEtOTBDMS, R$_2$=Et, R$_3$=Et

CLDS1 R$_1$=SBu, R$_2$=Me, R$_3$=EtOH

CLDS2 R$_1$=SEtOH, R$_2$=Et, R$_3$=Et

Scheme 1



CLD **CLDS1** **CLDS2**

Fig. 1

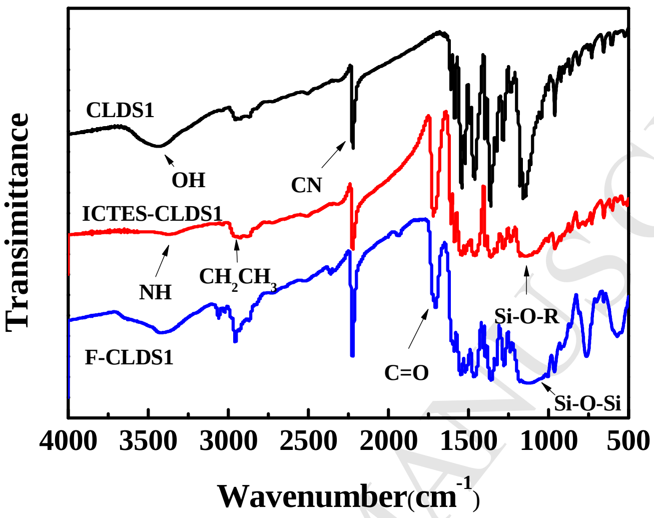

CLDS1
OH
CN
ICTES-CLDS1
NH
CH_2CH_3
Si-O-R
F-CLDS1
C=O
Si-O-Si
Transimittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm^{-1})

Fig. 2

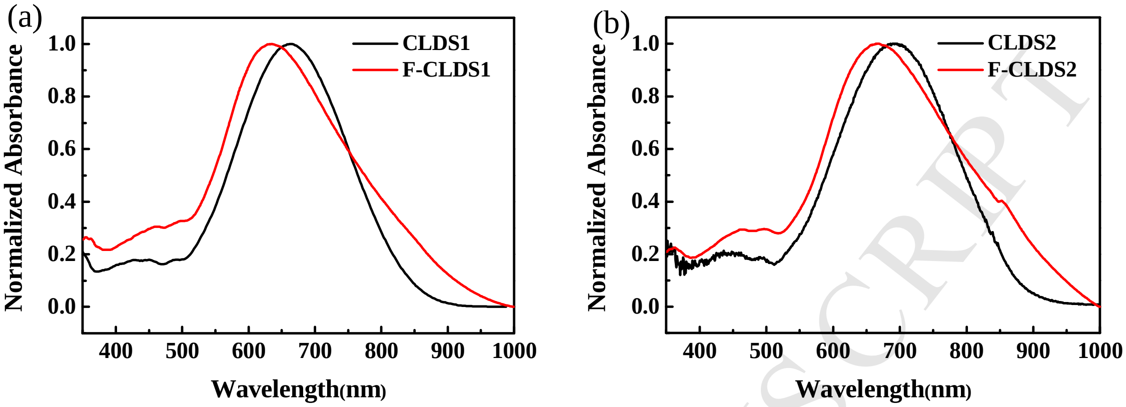

(a)
Normalized Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
900
1000
Wavelength(nm)
CLDS1
F-CLDS1
(b)
Normalized Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
900
1000
Wavelength(nm)
CLDS2
F-CLDS2

Fig. 3

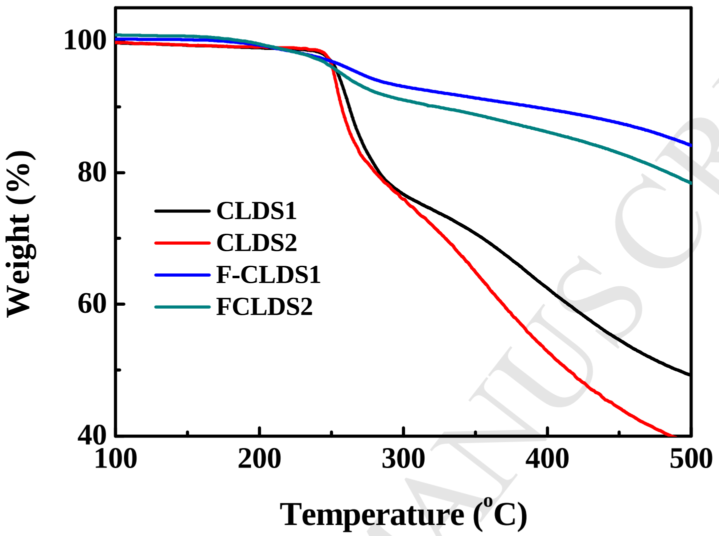

100
80
60
40
Weight (%)
100
200
300
400
500
Temperature (°C)
CLDS1
CLDS2
F-CLDS1
FCLDS2

Fig. 4

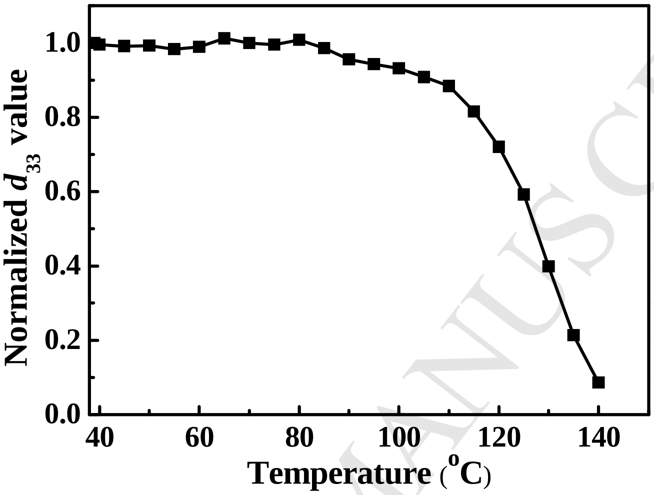

Normalized d_{33} value
1.0
0.8
0.6
0.4
0.2
0.0
40
60
80
100
120
140
Temperature (°C)

Fig. 5

Highlights

Two new phenyltetraene-based chromophores with alkylthio group were synthesized

Inorganic-organic hybrid films are prepared through sol-gel process

Incorporation of alkylthio group effectively improves the nonlinear optical property